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MELT PROCESSABLE ELECTRICALLY CONDUCTIVE POLYMERIC COMPOSITE AND  
METHOD OF PRODUCING SAME

[YOUYU KAKOU NO KANOU NA DOUDENSEI KOUBUNSHI FUKUGOUTAI OYABI  
SONO SEIZOU HOUHOU]

LI RUI-FENG et al.

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INVENTOR(S) (72) : Li Rui-Feng  
Li Chang-Zhen  
Wang -Hang

APPLICANT(S) (71) : Korea Research Institute of  
Chemical Technology

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[Scope of Claims]

[Claim 1] A method of producing a melt processable polyaniline composite excelling in electrical conductivity; which method is characterized in that an emeraldine base, obtained by dedoping a polyaniline or a polyaniline-derived salt, is caused to react with a protonic acid and then with an organic base, and is subsequently thermally treated.

[Claim 2] A method of producing a polyaniline composite according to Claim 1, characterized in that the aforementioned protonic acid is toluene sulfonic acid or dodecyl benzene sulfonic acid.

[Claim 3] A method of producing a polyaniline composite according to Claim 1, characterized in that the aforementioned organic base is trioctylamine.

[Claim 4] A method of producing a polyaniline composite according to Claim 1, characterized in that the surface acid level of the polyaniline composite to be neutralized using the aforementioned organic base is pH 4 ~ 7.

[Claim 5] A method of producing a polyaniline composite characterized in that, when producing the aforementioned emeraldine base in Claim 1, it is blended in an undried state in a solution with one or more dispersants selected from among polyethylene glycol, polyethylene glycol monomethyl ether,

dioctyl phthalate, polyvinyl alcohol and trioctylamine, and then dried to maintain an expanded state.

[Claim 6] A method of producing a polyaniline composite characterized in that, when producing the aforementioned emeraldine base in Claim 1, it is mechanically blended in an undried state with one or more dispersants selected from among polyethylene glycol, polyethylene glycol monomethyl ether, polyvinyl alcohol, dioctyl phthalate and trioctylamine, and then dried to maintain an expanded state.

[Claim 7] A polyaniline composite obtained by stirring to blend the emeraldine base, protonic acid and organic base in Claim 1, and then drying under reduced pressure.

[Claim 8] A polyaniline composite obtained by mechanically blending the emeraldine base, protonic acid and organic base in Claim 1, and then drying under reduced pressure.

[Claim 9] A polyaniline composite according to Claim 7 or 8, characterized in that the aforementioned protonic acid is toluene sulfonic acid or dodecyl benzene sulfonic acid.

[Claim 10] A polyaniline composite according to Claim 7 or 8, characterized in that the aforementioned organic base is trioctylamine.

[Claim 11] An electrically conductive polymer composite obtained by adding to the polyaniline composite, obtained in Claim 1, one or more thermoplastic resins selected from among low density

polyethylene, high density polyethylene, polypropylene, polyvinyl chloride or ethylene vinyl acetate and an antioxidant, such as tetrakis [methylene(3,5-di-tert-butyl-4-hydroxyhydrocinnamate)] methane, and then blending and heat processing.

[Detailed Description of the Invention]

[0001]

[Technical Field to Which the Invention Pertains] The present invention relates to melt processable electrically conductive polymeric composites and the methods of producing same. More specifically, the present invention relates to melt processable electrically conductive polymeric composites produced from polyaniline or a derivative thereof and methods of producing same.

[0002]

[Prior Art] Known electrically conductive polymeric substances frequently studied include polyanilines, polypyrroles and polythiophenes. Since these substances are easily polymerizable and excel in electrical conductivity, as well as oxidative stability, they are subject to continuous study. Of these electrically conductive polymeric substances, polyanilines are being studied the most due to their relative advantages in terms of price competitiveness, owing to the low price of its monomer aniline, and its significantly superior thermal stability.

[0003] Fields of application for polyanilines extend over a very wide range, including use as an electrode substance, an electromagnetic shielding material, a flexible electrode, an antistatic material, a corrosion proof coating agent and an electrochromic material. A polyaniline or a polyaniline derivative may be produced easily from aniline or an aniline derivative by an oxidative polymerization method. Structurally, polyanilines take on such forms as leucoemeraldine (or leucoemaraldine), emeraldine (or emaraldine) and pernigraniline, depending on the state of oxidization. Of the foregoing, polyanilines with the structural form of emeraldine are the most useful, since it has the highest electrical conductivity when doped and is stable in air.

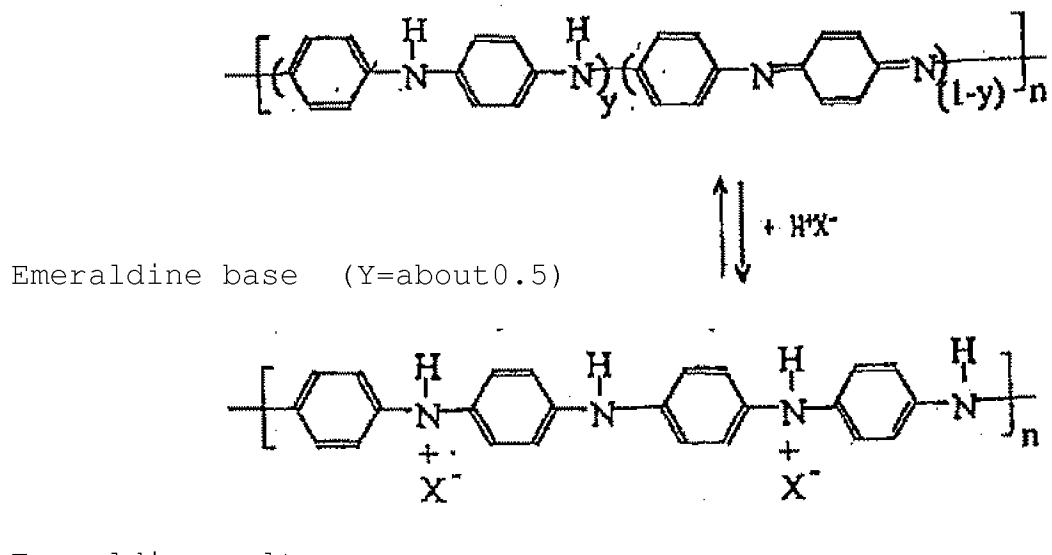
[0004] While a polyaniline with the structural form of an emeraldine base has a very low electrical conductivity at  $10^{-10}$  S/cm, the electrical conductivity can be increased to  $10^3$  S/cm by doping with a protonic acid, such as HCl, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, HClO<sub>4</sub>, HBH<sub>4</sub>, HPF<sub>6</sub>, phosphoric acid, organic sulfonic acid, picric acid and polymeric acid. Extensive study has already been conducted on the structure of an emeraldine base obtained by doping an emeraldine base with a protonic acid and on the resulting increase in electrical conductivity (U.S. Patent No. 3,963,498, U.S. Patent No. 4,025,463 and U.S. Patent No. 4,983,322).

[0005] Following are the structural formulas of polyanilines

having the structural forms of an emeraldine base and of a doped emeraldine base.

[Chemical 1]

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Emeraldine salt

[0006] One of the various methods developed to enhance melt processability is a method wherein processability is imparted on a polyaniline by subjecting it to a post polymerization process. In this case, a polyaniline is dispersed appropriately in a thermoplastic resin, using a highly refined polyaniline and a dispersant (Synth. Met. 15(1986)183; Synth. Met. 18(1987)671). However, the level of dispersion achieved by this method is low and, while satisfactory dispersion can be achieved in such resins as polyvinyl chloride (PVC), the level of dispersion in blends with other resins is low, rendering it difficult to produce an electrically conductive polymeric composite with

desirable electrical conductivity.

[0007] Still another method utilizes the fact that a neutral emeraldine base has high thermal stability to produce an electrically conductive polymeric composite by melt processing an emeraldine base and thermoplastic resin, which is processed into the required form, i.e., into a sheet or a fiber, and brought into contact with an appropriate protonic acid to impart electrical conductivity (European Unexamined Patent Publication No. 536,915 A2).

[0008] It is disclosed that blending with such resins as nylon 6, 6/6, 11, 12, polyethylene phthalate, polycarbonate, polyurethane and polycarolactone is made possible by this method. However, because this method involves bringing formed products into contact with a solution, in which a protonic acid is dissolved, to impart electrical conductivity to the electrically conductive polymeric composite, there is a variance in the level of electrical conductivity depending on the degree of acid dispersion within the polymeric composite, and bringing a formed product into contact with a protonic acid solution presents problems in terms of marring the appearance. Further, there also is the problem that it is not suitable for blending with the olefin resins, such as low density polyethylene (LDPE), high density polyethylene (HDPE) and polypropylene (PP), which are the most commonly used polymeric substances.

[0009] Another method recently disclosed enhances processability by taking advantage of the large size of the anion molecules that accept the protonic acid used to dope polyaniline. In fact, a polyaniline doped using dodecyl benzene sulfonic acid as a protonic acid, is known to be melt processable with LDPE, PP, HDPE, PVC and other resins. (U.S. Patent No. 5,232,631, International Unexamined Patent Publication No. 92/22911). Of the currently known methods, this method provides the best blend between polyaniline and thermoplastic resins.

[0010] However, should dodecyl benzene sulfonic acid be used in far greater amounts than necessary when doping an emeraldine base, while it is possible to produce a melt processable electrically conductive polyaniline composite, said polyaniline composite retains a stain at the time of contact and is obtained as a highly corrosive viscous fluid. Such fluid with flowability is not suitable for melt processing. Further, an excess of highly corrosive sulfonic acid will be present in the final electrically conductive polymeric composite, and the use of a highly corrosive material entails a very large problem when taking into consideration the fact that an electrically conductive polymeric composite comprising such electrically conductive polymer is ultimately employing in an electronic device.

[0011] In order to remedy this problem, a method was developed

to solidify a fluid polyaniline composite doped with dodecyl benzene acid by heat treating at 40 ~ 220°C (European Patent No. 545,279). Since a polyaniline composite thus solidified can be produced as a powder or granules, it is much easier to handle in the process of common melt processing.

[0012] Further, a method has been developed wherein a substance, such as ZnO, Na<sub>2</sub>CO<sub>3</sub> and CaCO<sub>3</sub>, is used together to maintain electrical conductivity while neutralizing the excess acid present (European Examined Patent Publication No. 627,746 A1; European Examined Patent Publication No. 627,745 A1). In this case, there is the problem that it is difficult to adjust the extent to which the base is dispersed in the polymer, since a solid base is used, and the CO<sub>2</sub> generated in the neutralization poses a problem to the process. Further, it has been observed that the electrical conductivity of a polyaniline reduced by about 100 times, which reduction in electrical conductivity results in a considerable decline in the efficiency of electrically conductive polymers

[0013]

[Problems to Be Solved by the Invention] Because a doped polyaniline is electrically charged, polymer chains to interact intensively, causing a decline in processability and placing numerous limitations on its practical usefulness. In fact, while a neutral emeraldine base is known to dissolve in a polar

organic solvent, be stable even at a temperature of 200°C or higher, and be melt processable to a certain extent; an emeraldine salt with electrical conductivity imparted thereon does not dissolve

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in an organic solvent, thermally decomposes at a temperature of 200°C or lower, and is not suitable for melt processing. This is to say that it cannot be used in methods involving dissolution in a solvent and melt processing, which are the plastic processing methods generally used. Hence, solving the foregoing is the most important in putting an electrically conductive polymeric substance to practical use.

[0014] In particular, in view of the fact that the biggest advantage a polymeric substance has is that its suitability for mass production using such processing method as compression, extrusion, and injection molding, the enhancement of processability, particularly melt processability, is the most important problem to be solved in putting polyanilines to practical use.

[0015] The object of the present invention is to provide a method of producing a polyaniline composite that exists as a solid at ambient temperature, is easy to handle during processing, the surface acid level (pH) falls within the range of 4 ~ 7 and has electrical conductivity of  $10^{-10} \sim 10^1$  S/cm

(particularly  $10^{-1} \sim 10^1$  S/cm). Another object of the present invention is to provide a method of producing an electrically conductive polyaniline composite with high electrical conductivity, being well dispersed within a polymeric composite which can be produced with ease by a melt processing method employing a common thermoplastic resin. Another object of the present invention is to provide a method of producing an electrically conductive polymeric composite having high electrical conductivity by melt processing a polyaniline composite with a common thermoplastic resin.

[0016]

[Means for Solving the Problem] As a result of devoted studies to resolve the foregoing problems, the present inventors found that using an organic base (particularly an organic amine, such as alkyl amine) to neutralize the excess organic acid resulted in a negligible decline in electrical conductivity; finding also that a superior level of dispersion is achieved in the subsequent melt processing when an emeraldine base is swollen with a solvent at the time of production of the polyaniline composite, and also invented a method of maintaining an emeraldine base in a swollen state during the production of a polyaniline composite; and thus completed the invention relating to a melt processable polyaniline composite having superior electrical conductivity with a pH in the 4 ~ 7 range, an

electrically conductive polymeric composite employing same, and a method of producing both.

[0017] The present invention provides a method of producing a melt processable polyaniline composite excelling in electrical conductivity; the method, which is characterized in that an emeraldine base, obtained by dedoping a polyaniline or a polyaniline-derived salt, is caused to react with a protonic acid and then with an organic base, and is subsequently thermally treated. The protonic acid used in the present invention may be hydracid, for example.

[0018] A polyaniline composite according to the present invention may be produced by the following two methods.

Method 1

1) Producing a Polyaniline Salt

A doped polyaniline was synthesized by preparing 1 liter of an aqueous solution containing 0.05 ~ 1 M of aniline; adding to the aforementioned aqueous aniline solution 0.3 ~ 1 M of a protonic acid, such as hydracid and generally HCl, and 0.5 M ~ 1.5 M of ammonium persulfate, as an antioxidant, over a period of 1 ~ 2 hours at a temperature of -10 ~ 0°C; incubating the resulting blend sufficiently for 30 minutes ~ 24 hours at a temperature of -10 ~ 80°C; and filtering out the polyaniline generated. The polyaniline thus synthesized was cleansed with distilled water

and methanol, and excess solvent is removed by filtering under reduced pressure. Care must be exercised when cleansing and filtering to prevent the polyaniline from drying. Care should be exercised since allowing the polyaniline to dry completely at this time will result in reduced dispersability in the subsequent melt processing, even if the same method is used.

[0019] 2) Producing an Emeraldine Base by Dedoping

A polyaniline doped with protonic acid, i.e. an emeraldine salt, was dedoped by neutralizing with an aqueous base solution. While NaOH, Na<sub>2</sub>CO<sub>3</sub>, NH<sub>4</sub>OH, Et<sub>3</sub>N or any other base that dissolves well in water may be used as the base at this time, Na<sub>2</sub>CO<sub>3</sub>, NH<sub>4</sub>OH and Et<sub>3</sub>N may be used most effectively. The doped polyaniline produced in step 1) above was added to an aqueous solution having 1% ~ 20% of an aforementioned base dissolved therein, the blend generated was caused to react for 30 minutes ~ 24 hours, and the dedoped aniline, i.e. an emeraldine base, was filtered out under reduced pressure. The filtered-out emeraldine base was cleansed with distilled water and methanol. Here again, care should be exercised appropriately to keep the filtered-out emeraldine base from drying completely.

[0020] 3) Producing an Emeraldine Base Suitable for Dispersion

An emeraldine in a slightly swollen state was blended well for about 1 hour ~ 3 hours with a 2 ~ 10 weight % solution of one or more dispersants selected from among polyethylene glycol (PEG),

polyethylene glycol monomethyl ether (PEG-OMe), polyvinyl alcohol (PVA), dioctyl phthalate (DOP) and organic alkyl amine. While alcohols having 1 ~ 5 carbon atoms of water may be used as the solvent, ethanol is the most useful of the foregoing. The blend generated was vacuum dried to produce an emeraldine base having an aforementioned dispersant well dispersed therein.

[0021] 4) Producing a Polyaniline Composite by Doping

The emeraldine based produced above was mixed well with the aforementioned sulfonic acid at a rate of 1.5 sulfonic acid equivalent to 1 nitrogen (in the polyaniline) equivalent. As for the method of mixing at this time, they were dispersed in ethanol and caused to react for 4 ~ 24 hours at 40 ~ 70°C to obtain a dark green doped polyaniline. Organic alkyl amine corresponding to the amount of excess acid was added thereto to neutralize the excess acid and stirred for 1 hour ~ 2 hours. The solvent was removed from the

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aforementioned disperse solution under reduced pressure to produce a polyaniline composite. The aforementioned solvent was removed under reduced pressure to obtain a polyaniline composite.

[0022] 5) Solidifying a Polyaniline Composite

Although the polyaniline composite produced by the foregoing method is obtained as a highly viscous fluid, the fluid

solidifies when cured at about 50 ~ 150°C, becoming easier to handle and undergoing an increase in electrical conductivity. The electrical conductivity of the polyaniline composite was within a  $10^{-1}$  ~  $10^1$  S/cm range.

[0023] Method 2

Steps 1) and 2) of Method 2 were performed in the same manner as steps 1) and 2) in abovementioned Method 1.

3) Producing an Emeraldine Based with Satisfactory Dispersability

Using a ball mill, a Brabender mixer or a banbury mixer, undried emeraldine, in a moist state, was mechanically blended with about 5 ~ 20 weight %, one or more from among polyethylene glycol, polyethylene glycol monomethyl ether, polyvinyl alcohol, dioctyl phthalate and organic alkyl amine. In this case, there is the advantage that there is no need to use a solvent. The emeraldine base with satisfactory dispersability produced is vacuum dried.

[0024] 4) Producing a Polyaniline Composite by Doping

An organic sulfonic acid and an organic alkyl amine, which is necessary to neutralize the excess organic sulfonic acid, were added to the emeraldine base produced in step 3) above and mechanically blended directly using a ball mill, a Brabender mixer or a banbury mixer. A doped polyaniline composite was obtained in the form of a viscous fluid.

[0025] 5) Solidifying a Polyaniline Composite

This was done in the same manner as in Method 1 above. While examples of the organic sulfonic acid that may be used here include alkyl sulfonic acids having 1 ~ 12 carbon atoms and such alkyl benzene sulfonic acids as toluene sulfonic acid and benzene sulfonic acid, alkyl benzene sulfonic acid is desirable of the foregoing; in particular, toluene sulfonic acid and dodecyl benzene sulfonic acid were the most desirable in generating a polyaniline composite with the best electrical conductivity. Further, it is possible to use tertiary amines having 2 ~ 12 carbon atoms as the organic amine, and the most advantageous among them in terms of thermal stability and price include tributylamine, trioctylamine, triisobutylamine, triisooctylamine and triisododecylamine.

[0026] The advantage of Method 1 is that because the doping reaction takes place in a solution, the polyaniline composite produced is completely doped and excels in electrical conductivity. The advantage of Method 2 is that it is suitable for mass production, though there is a slight decline in electrical conductivity due to the use of a mechanical blending method, which is practical for use in mass production. The polyaniline composites produced by applying the aforementioned methods, etc., were all melt processable with ethylene vinyl acetate (EVA) resins, LDPE, HDPE, PP, PPV and the like using the

following method.

[0027] A desirable ratio of a polyaniline composite and an EVA resin or LDPE, and 0.1 wt. % of tetrakis [methylene (3,5-di-tert-butyl-4-hydroxyhydrocinnamate)] methane (IR 1010), as an antioxidant, were combined and blended using a Brabender mixer or a banbury mixer for 5 ~ 30 minutes at about 50 ~ 90 rpm at a temperature of about 140 ~ 180°C. Optimum results were obtained when blended for 10 minutes at 80 rpm at 150°C.

[0028] Two methods were used to obtain electrically conductive polymeric composites from high density polyethylenes and polyaniline composites. First, a polyaniline composite and a low density polyethylene were produced using a method described above, which were then blended with a high density polyethylene for 10 minutes at a speed of 60 rpm at 180 ~ 200°C to obtain an electrically conductive polymeric composite. In this case, although the decomposition temperature of a polyaniline is about 200°C, it was possible to obtain the effect of enhanced thermal stability when an electrically conductive polymeric composite was pre-produced using a low density polyethylene.

[0029] In another method, an electrically conductive polymeric composite was produced by directly combining a desirable ratio of a polyaniline composite and a high density polyethylene and blending for 5 minutes at a rate of 60 rpm at 190 ~ 200°C. A polyaniline composite produced by this method was observed to be

stable for about 10 ~ 20 minutes at 200°C. After combining a desirable ratio of polyvinyl chloride, to which a polyaniline composite and such substances as a plasticizer have been added, the resulting blend was blended for 10 minutes at a rate of 30 rpm at 160°C to obtain an electrically conductive polyvinyl chloride composite.

[0030] A characteristic of the present invention lies in the fact that when an emeraldine base is produced, it is blended together with a dispersant prior to drying, thereby rendering it possible to produce an polyaniline composite far superior in dispersability to polyaniline composites produced by other methods. As a result, it is possible to achieve a far superior dispersion effect, as compared with polyaniline composites produced by other methods, when melt processing with a thermoplastic resin. Dispersability in the polymeric composite form is very important, as it relates directly to the electrical conductivity of the ultimate electrically conductive polymeric composite.

[0031] Another advantage of the present invention is that it is possible to maintain the acid level in the 5 ~ 7 range by using an organic alkyl amine base in lieu of an inorganic base to neutralize the excess inorganic sulfonic acid and produce a polyaniline composite with electrical conductivity of  $10^{-1} \sim 10^1$  S/cm. Further, since the organic alkyl amine used combines

dispersing action, a synergistic effect can be achieved. Another advantage of the present invention is that because it is possible by thermal processing to solidify the polyaniline composite, which has been neutralized using an organic base, it can be handled with ease in processing and is very useful in terms of practical applications.

[0032] These polyaniline composites and electrically conductive polymeric composites may be used for such applications as antistatic materials, electromagnetic shielding materials, electrode substances for secondary

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batteries, sensors, electrically conductive coating, plastic heating materials, plastic switches and anti-corrosion coating. In particular, they have the advantage of being lighter and superior in mechanical properties to metals and inorganic semiconductor materials, and lower in synthesizing and processing costs.

[0033]

[Working Example] The present invention is described in greater detail hereinafter with reference to non-limiting working examples.

Working Example 1 Producing an Emeraldine Base  
600 ml of an aqueous solution, in which 228 g of ammonium persulfate, was gradually dripped into 1 liter of an aqueous

solution, in which 93 g of aniline and 87 ml of 35% aqueous hydrochloric acid solution, over a period of 3 hours at 0°C. Following completion of the drip, the resulting blend was caused to react for 12 hours while mechanically stirring, and the polyaniline precipitated that out was collected by filtering under reduced pressure. The polyaniline filtered was suspended in 3 liters of distilled water while stirring sufficiently, and then filtered again. This process was repeated two times, cleansed with 4 liters of acetone, and subsequently cleansed again with 1 liter of distilled water.

[0034] Before drying the polyaniline thus cleansed, 10 liters of 0.5 ~ 1% aqueous ammonium solution was added and stirred sufficiently for about 10 hours. A polyaniline thus reacted and dedoped, i.e. an emeraldine base, was filtered and collected under reduced pressure. The filtered emeraldine base was sequentially cleansed with 10 liters of distilled water, 4 liters of acetone and 1 liter of propyl alcohol. The emeraldine based was dried completely after cleansing.

[0035] Working Example 2 Producing an Emeraldine Base  
The same method as in Working Example 1 was used, with the exception of dispersing a moist-state polyaniline, prior to drying, in 100 ml of an ethanol solution in which one or more from among polyethylene glycol, polyethylene glycol monomethyl ether (molecular weight of 20,000), dioctyl phthalate, polyvinyl

alcohol and trioctylamine have been dissolved in an amount of about 10 weight %, and stirring the resulting blend sufficiently for about 3 hours. The blend was dried under reduced pressure to produce an emeraldine base composite containing a dispersant(s).

[0036] Working Example 3 Producing an Emeraldine Base

The same method as in Working Example 1 was used, with the exception of dispersing a moist-state polyaniline, prior to drying, in about 10 weight % of one or more dispersants from among polyethylene glycol, polyethylene glycol monomethyl ether (molecular weight of 20,000), dioctyl phthalate, polyvinyl alcohol and trioctylamine and mechanically blending the resulting blend. The blend was dried under reduced pressure to produce an emeraldine base composite containing a dispersant(s).

[0037] Working Example 4 Producing a Polyaniline Composite

Toluene sulfonic acid or dodecyl benzene sulfonic acid was added to the emeraldine based produced in Working Example 1 at a ratio of 1.5:1 (molar ratio of aniline monomers present in the toluene sulfonic acid and the polyaniline) and blended well. As a method of blending at this time, a 20 wt % ethanol dispersion liquid was prepared and caused to react for 12 hours at 50°C to obtain a dark green doped polyaniline, trioctylamine was added thereto in an amount equal to 1 mole equivalent of aniline monomer to neutralize the excess acid, and the resulting blend was stirred again for 1 hour. The solvent was removed from the dispersion

liquid under reduced pressure to obtain a highly viscous fluid, and the fluid solidified when heat treated at 80 ~ 100°C, becoming easier to handle while the electrical conductivity also increased. The electrical conductivity of the polyaniline composite thus produced was 0.5 S/cm.

[0038] Working Example 5 Producing a Polyaniline Composite  
A polyaniline composite was produced using the emeraldine base produced in Working Example 2 and employing the method used in Working Example 4. The electrical conductivity of the polyaniline composite was 1 S/cm.

Working Example 6 Producing a Polyaniline Composite  
A polyaniline composite was produced using the emeraldine base produced in Working Example 3 and employing the method as in Working Example 4. The electrical conductivity of the polyaniline composite was 0.3 S/cm.

[0039] Working Example 7 Producing a Polyaniline Composite  
Dodecyl benzene sulfonic acid or toluene sulfonic acid (1.5 times the number of moles of aniline monomers present in the polyaniline) was added to the emeraldine base produced in Working Example 1 and blended using a ball mill, a Brabender mixer or a banbury mixer. Trioctylamine was added thereto to neutralize excess acid, and then blended. At this time, the same results were obtained when doping the emeraldine base first with an acid and then adding the amine, and when adding the acid and

the amine simultaneously to dope the emeraldine base. The highly viscous fluid thus obtained was solidified by heat treating at 80°C. The electrical conductivity of the polyaniline composite obtained was 1 ~ 10 S/cm.

[0040] Working Example 8 Producing a Polyaniline Composite  
The emeraldine base produced in Working Example 2 was used to obtain a polyaniline employing the same method as in Working Example 7. The electrical conductivity of the polyaniline composite was 1 S/cm.

Working Example 9 Producing a Polyaniline Composite  
The emeraldine base produced in Working Example 3 was used to obtain a polyaniline employing the same method as in Working Example 7. The electrical conductivity of the polyaniline composite was 0.5 S/cm.

[0041] Comparative Example 1

The emeraldine obtained in Working Example 1 was mechanically blended with dodecyl benzene sulfonic acid, equal to 1.5 times the number of moles of aniline monomers present in the polyaniline, to obtain a highly viscous fluid, which fluid was heat treated at 80°C and solidified. The electrical conductivity of the polyaniline composite obtained at this time was 5 S/cm.

[0042] Comparative Example 2

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Although the same method was used as in Working Example 4, CaCO<sub>3</sub>

or ZnO was used in lieu of trioctylamine to obtain a polyaniline composite. The electrical conductivity of the polyaniline composite was  $10^{-3}$  S/cm.

[0043] Comparative Example 3

Although the same method was employed as in Working Example 4, toluene sulfonamide was used in lieu of trioctylamine to obtain a polyaniline composite. The electrical conductivity of the polyaniline composite was 0.1 S/cm. However, this composite decomposed at about 150°C, rapidly losing electrical conductivity.

[0044] Working Example 10

The polyaniline composite produced in Working Example 4 or 7 was combined with a low density polyethylene at a desirable ratio, together with 0.1 wt % of IR 1010 as an antioxidant, and the resulting blend was blended using a Brabender mixer or a banbury mixer for 10 minutes at a rate of 50 ~ 90 rpm at 150°C. After the electrically conductive polymeric composite obtained was compressed and made into a film using a thermal compressor, the electrical conductivity of the electrically conductive polymeric composite and the surface pH of the film, according to the polyaniline composite content, were measured. The results are shown in Table 1 below.

[0045] Working Example 11

An electrically conductive polymeric composite was produced

using the polyaniline composite produced in Working Example 5 or 8 employing the same method as in Working Example 10. The electrical conductivity of the electrically conductive polymeric composite and the surface pH of the film, according to the polyaniline composite content, are shown in Table 1 below.

#### Working Example 12

An electrically conductive polymeric composite was produced using the polyaniline composite produced in Working Example 6 or 9 employing the same method as in Working Example 10. The electrical conductivity of the electrically conductive polymeric composite and the surface pH of the film, according to the polyaniline composite content, are shown in Table 1 below.

#### [0046] Working Example 13

An electrically conductive polymeric composite was produced using the polyaniline composite produced in Comparative Example 1 employing the same method as in Working Example 10. The electrical conductivity of the electrically conductive polymeric composite and the surface pH of the film, according to the polyaniline composite content, are shown in Table 1 below.

#### Working Example 14

An electrically conductive polymeric composite was produced using the polyaniline composite produced in Comparative Example 2 employing the same method as in Working Example 10. The electrical conductivity of the electrically conductive polymeric

composite and the surface pH of the film, according to the polyaniline composite content, are shown in Table 1 below.

[0047] Working Example 15

An electrically conductive polymeric composite was produced using the polyaniline composite produced in Comparative Example 3 employing the same method as in Working Example 10. The electrical conductivity of the electrically conductive polymeric composite and the surface pH of the film, according to the polyaniline composite content, are shown in Table 1 below.

[0048]

[Table 1]

Table 1 Properties of Low Density Polyethylene and Polyaniline Composite Blends

| 使われた<br>複合体の種類 | ポリアニリン複合体の含量による電導度 <sup>1)</sup> とpH <sup>2)</sup> |                      |                      |                        |                      |                      |
|----------------|--|----------------------|----------------------|------------------------|----------------------|----------------------|
|                | 0.5wt%   | 2wt%                 | 5wt%                 | 10wt%                  | 20wt%                | 30wt%                |
| 実施例 4          | 10 <sup>-9</sup> (7)                               | 10 <sup>-7</sup> (7) | 10 <sup>-5</sup> (7) | 10 <sup>-4</sup> (7)   | 0.06 (6)             | 0.1 (5)              |
| 実施例 5          | 10 <sup>-9</sup> (7)                               | 10 <sup>-7</sup> (7) | 10 <sup>-5</sup> (7) | 10 <sup>-4</sup> (7)   | 10 <sup>-3</sup> (6) | 0.08 (5)             |
| 実施例 6          | 10 <sup>-8</sup> (7)                               | 10 <sup>-6</sup> (7) | 10 <sup>-4</sup> (7) | 6×10 <sup>-3</sup> (7) | 0.08 (6)             | 0.8 (5)              |
| 実施例 7          | 10 <sup>-8</sup> (7)                               | 10 <sup>-6</sup> (7) | 10 <sup>-4</sup> (7) | 10 <sup>-3</sup> (7)   | 0.08 (6)             | 0.7 (5)              |
| 実施例 8          | 10 <sup>-4</sup> (7)                               | 10 <sup>-6</sup> (7) | 10 <sup>-4</sup> (7) | 6×10 <sup>-3</sup> (7) | 0.06 (6)             | 0.5 (5)              |
| 実施例 9          | 10 <sup>-8</sup> (7)                               | 10 <sup>-6</sup> (7) | 10 <sup>-4</sup> (7) | 6×10 <sup>-3</sup> (7) | 0.06 (6)             | 0.5 (5)              |
| 比較例 1          | 10 <sup>-8</sup> (7)                               | 10 <sup>-6</sup> (6) | 10 <sup>-4</sup> (6) | 10 <sup>-3</sup> (5)   | 10 <sup>-2</sup> (4) | 0.05 (3)             |
| 比較例 2          | <10 <sup>-9</sup> (7)                              | 10 <sup>-8</sup> (7) | 10 <sup>-7</sup> (7) | 10 <sup>-6</sup> (7)   | 10 <sup>-5</sup> (7) | 10 <sup>-3</sup> (6) |
| 比較例 3          | 10 <sup>-9</sup> (7)                               | 10 <sup>-7</sup> (6) | 10 <sup>-5</sup> (6) | 10 <sup>-4</sup> (5)   | 10 <sup>-3</sup> (5) | 0.01 (5)             |

Notes: 1) The unit for electrical conductivity is S/cm, and 2) the pH is indicated in () .

\* The pH was measured by placing a drop of water on the surface of the film, allowing the drop to stand for 5 minutes, and then measuring the pH of the drop of the water using litmus paper.

Electrical Conductivity<sup>1)</sup> and pH<sup>2)</sup> According to Polyaniline Composite Content

Type of Composite Used

Working Example 4  
Working Example 5  
Working Example 6  
Working Example 3  
Working Example 8  
Working Example 9  
Comparative Example 1  
Comparative Example 2  
Comparative Example 3

[0049] Working Example 16

30 wt % of the polyaniline composites produced in Working Examples 10 ~ 12 were combined with a low density polyethylene or a high density polyethylene at a desirable ratio and blended for 10 minutes at a rate of 60 rpm at 180 ~ 200°C to obtain electrically conductive polymeric composites. The electrical conductivity and the surface pH of the films produced from the electrically conductive polymeric composites are shown in Table 2 below.

[0050] Working Example 17

After combining the polyaniline composite produced in Working Example 4 or 7 with a high density polyethylene at a desirable ratio, the resulting mixture was blended for 5 minutes at a rate of 60 rpm at 190 ~ 200°C to obtain an electrically conductive polymeric composite. The electrical conductivity and the surface pH of the film produced from the electrically conductive

Polymer composite are shown in Table 2 below.

[0051] Working Example 18

After combining the polyaniline composite produced in Working Example 5 or 8 with a high density polyethylene at a desirable ratio, the resulting mixture was blended for 5 minutes at a rate of 60 rpm at 190 ~ 200°C to obtain an

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electrically conductive polymeric composite. The electrical conductivity and the surface pH of the film produced from the electrically conductive polymeric composite are shown in Table 2 below.

[0052] Working Example 19

After combining the polyaniline composite produced in Working Example 6 or 9 with a high density polyethylene at a desirable ratio, the resulting mixture was blended for 5 minutes at a rate of 60 rpm at 190 ~ 200°C to obtain an electrically conductive polymeric composite. The electrical conductivity and the surface pH of the film produced from the electrically conductive polymeric composite are shown in Table 2 below.

[0053]

[Table 2]

Table 2 Properties of High Density Polyethylene and Polyaniline Composite Blends

| 使われた<br>複合体の種類      | ポリアニリン複合体の含量による電導度 <sup>1)</sup> とpH <sup>2)</sup> |               |               |               |           |
|---------------------|--|---------------|---------------|---------------|-----------|
|                     | 0.5wt%   | 2wt%          | 5wt%          | 10wt%         | 20wt%     |
| 実施例10 <sup>3)</sup> | $10^{-4}$ (7)                                      | $10^{-6}$ (7) | -             | -             | -         |
| 実施例11 <sup>3)</sup> | $10^{-4}$ (7)                                      | $10^{-6}$ (7) | -             | -             | -         |
| 実施例12 <sup>3)</sup> | $10^{-4}$ (7)                                      | $10^{-6}$ (7) | -             | -             | -         |
| 実施例4, 7             | $10^{-3}$ (7)                                      | $10^{-6}$ (7) | $10^{-5}$ (7) | $10^{-4}$ (6) | 0.005 (6) |
| 実施例5, 8             | $10^{-3}$ (7)                                      | $10^{-6}$ (7) | $10^{-5}$ (7) | $10^{-4}$ (6) | 0.01 (6)  |
| 実施例6, 9             | $10^{-4}$ (7)                                      | $10^{-6}$ (7) | $10^{-5}$ (7) | $10^{-4}$ (6) | 0.02 (6)  |

Notes: 1) The unit for electrical conductivity is S/cm, and 2) the pH is indicated in () .

3) A low density polyethylene containing 30 wt % of the polyaniline produced in the corresponding Working Example was used in the blend. The polyaniline composite content indicated is the polyaniline composite content of the final blend.

#### Electrical Conductivity<sup>1)</sup> and pH<sup>2)</sup> According to Polyaniline Composite Content

##### Type of Composite Used

Working Example 10<sup>3)</sup>

Working Example 11<sup>3)</sup>

Working Example 12<sup>3)</sup>

Working Examples 4, 7

Working Examples 5, 8

Working Examples 6, 9

#### [0054] Working Example 20

After combining the polyaniline composite produced in Working Example 4 or 7 with polypropylene at a desirable ratio, the resulting mixture was blended for 5 minutes at a rate of 60 rpm at 190 ~ 200°C to obtain an electrically conductive polymeric composite. The electrical conductivity and the surface pH of the film produced from the electrically conductive polymeric composite are shown in Table 3 below.

[0055] Working Example 21

After combining the polyaniline composite produced in Working Example 5 or 8 with polypropylene at a desirable ratio, the resulting mixture was blended for 5 minutes at a rate of 60 rpm at 190 ~ 200°C to obtain an electrically conductive polymeric composite. The electrical conductivity and the surface pH of the film produced from the electrically conductive polymeric composite are shown in Table 3 below.

[0056] Working Example 22

After combining the polyaniline composite produced in Working Example 6 or 9 with polypropylene at a desirable ratio, the resulting mixture was blended for 5 minutes at a rate of 60 rpm at 190 ~ 200°C to obtain an electrically conductive polymeric composite. The electrical conductivity and the surface pH of the film produced from the electrically conductive polymeric composite are shown in Table 3 below.

[0057]

[Table 3]

Table 3 Properties of Polypropylene and Polyaniline Composite Blends

| ポリアニリン複合体の含量による電導度 <sup>1)</sup> とpH <sup>2)</sup> |               |                        |               |                        |           |
|--|---------------|------------------------|---------------|------------------------|-----------|
| 使われた<br>複合体の種類                                     | 0.5wt%        | 2wt%                   | 5wt%          | 10wt%                  | 20wt%     |
| 実施例4、7   | $10^{-9}$ (7) | $5 \times 10^{-8}$ (7) | $10^{-6}$ (7) | $5 \times 10^{-5}$ (6) | 0.008 (6) |
| 実施例5、8   | $10^{-9}$ (7) | $10^{-7}$ (7)          | $10^{-5}$ (7) | $2 \times 10^{-4}$ (6) | 0.01 (6)  |
| 実施例6、9   | $10^{-9}$ (7) | $10^{-7}$ (7)          | $10^{-5}$ (7) | $5 \times 10^{-4}$ (6) | 0.05 (6)  |

Notes: 1) The unit for electrical conductivity is S/cm, and 2)

the pH is indicated in () .

### Electrical Conductivity<sup>1)</sup> and pH<sup>2)</sup> According to Polyaniline Composite Content

Type of Composite Used

Working Examples 4, 7

Working Examples 5, 8

Working Examples 6, 9

[0058] Working Example 23

The polyaniline composites produced in Working Examples 4 ~ 9 were combined at a desirable ratio with polyvinyl chloride (PVC) blended in advance with a plasticizer, a stabilizer, an antioxidant and other agents, and the resulting mixture was blended for 10 minutes at a rate of 30 rpm at 160°C to obtain an electrically conductive polymeric composites. The electrical conductivity and the surface pH of the films produced from the electrically conductive polymeric composites are shown in Table 4 below.

[0059]

[Table 4]

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Table 4 Properties of Polyvinyl Chloride and Polyaniline Composite Blends

| 使われた<br>複合体の種類 | ポリアニリン複合体の含量による電導度 <sup>1)</sup> とpH <sup>2)</sup> |               |               |                        |       |
|----------------|--|---------------|---------------|------------------------|-------|
|                | 0.5wt%   | 2wt%          | 5wt%          | 10wt%                  | 30wt% |
| 実施例4、7         | $10^{-4}$ (7)                                      | $10^{-6}$ (7) | $10^{-5}$ (7) | $5 \times 10^{-2}$ (6) | 1(5)  |
| 実施例5、8         | $10^{-4}$ (7)                                      | $10^{-6}$ (7) | $10^{-4}$ (7) | $10^{-2}$ (6)          | 5(5)  |
| 実施例6、9         | $10^{-3}$ (7)                                      | $10^{-6}$ (7) | $10^{-4}$ (7) | $10^{-2}$ (6)          | 3(5)  |

Notes: 1) The unit for electrical conductivity is S/cm, and 2)

the pH is indicated in () .

#### Electrical Conductivity<sup>1)</sup> and pH<sup>2)</sup> According to Polyaniline Composite Content

Type of Composite Used

Working Examples 4, 7

Working Examples 5, 8

Working Examples 6, 9

#### [0060] Working Example 24

The polyaniline composites produced in Working Examples 4 ~ 9 were combined at a desirable ratio with ethylene vinyl acetate (EVA) and, after adding 0.1 wt % of IR 1010 thereto as an antioxidant, the resulting mixture was blended using a Brabender mixer or a banbury mixer for 10 minutes at a rate of 50 ~ 90 rpm at 150°C. After the electrically conductive polymeric composite produced was compressed and made into a film using a thermal compressor, the electrical conductivity of the electrically conductive polymeric composite and the surface pH of the film, according to the polyaniline composite content, were measured.

The results are shown in Table 5 below. The electrical conductivity and the pH of the EVA composites resembled the electrical conductivity and pH of each and every polyaniline composites.

#### [0061]

#### [Table 5]

Table 5 Properties of EVA Resin and Polyaniline Composite Blends

| ポリアニリン複合体の含量による電導度 <sup>1)</sup> とpH <sup>2)</sup> |               |               |               |                        |       |
|--|---------------|---------------|---------------|------------------------|-------|
| 使われた<br>複合体の種類                                     | 0.5wt%        | 2wt%          | 5wt%          | 10wt%                  | 30wt% |
| 実施例4、7   | $10^{-4}$ (7) | $10^{-5}$ (7) | $10^{-5}$ (7) | $5 \times 10^{-2}$ (6) | 1(5)  |
| 実施例5、8   | $10^{-4}$ (7) | $10^{-6}$ (7) | $10^{-4}$ (7) | $10^{-2}$ (6)          | 5(5)  |
| 実施例6、9   | $10^{-4}$ (7) | $10^{-6}$ (7) | $10^{-4}$ (7) | $10^{-2}$ (6)          | 3(5)  |

Notes: 1) The unit for electrical conductivity is S/cm, and 2) the pH is indicated in () .

#### Electrical Conductivity<sup>1)</sup> and pH<sup>2)</sup> According to Polyaniline Composite Content

Type of Composite Used

Working Examples 4, 9

Working Examples 5, 8

Working Examples 6, 9

[0062]

[Effect of the Invention] It was confirmed from the foregoing working examples that the present invention excels as a method of producing electrically conductive polymeric composites with high electrical conductivity, regardless of the small amount of polyaniline composites contained, by melt processing polyaniline composites, which are essentially electrically conductive polymers, with a thermal plastic resin, particularly such resins as polyolefin and polyvinyl chloride resins. These electrically conductive polymeric composites may be used as antistatic materials (range of electrical conductivity required:  $10^{-9} \sim 10^{-4}$  S/cm), in addition to such other uses as anti-corrosion materials, electrode substances for secondary batteries, electromagnetic shield materials.